Pd/C-catalyzed practical degradation of PCBs at room temperature

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Abstract

The catalytic degradation method of polychlorinated biphenyls (PCBs) using the palladium on activated carbon–triethylamine (Pd/C–Et$_3$N) system under ambient hydrogen pressure and temperature was developed. Aroclor® 1254, Aroclor® 1248, 10% Aroclor® 1254 in paraffin oil and PCBs from capacitor could be completely dechlorinated to afford biphenyl and Et$_3$N·HCl. Fifteen pure PCB congeners, including the highly toxic co-planar PCBs, were smoothly dechlorinated to biphenyl within 1 or 2 h using 10% Pd/C (10% of substrate weight) and Et$_3$N (1.2 equiv. vs. Cl numbers). However, the dechlorination of the fully *ortho*-substituted PCB congeners was delayed and chlorine atoms on the *ortho*-positions still remained under the hydrogenation conditions, but these PCB congeners are only slightly present in the commercial PCB mixture. The Pd/C–Et$_3$N–H$_2$ system offers a simple, safe, and inexpensive degradation method of PCBs under mild reaction conditions.
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1. Introduction

Polychlorinated biphenyls (PCBs), which consist of 209 congeners with different numbers and positions of chlorine atoms on a biphenyl nucleus, were commercially produced from 1929 to the mid-1970s and used all over the world mainly as lubricants and coolants in transformers, capacitors, and other electrical equipment. However, their hydrophobic property as well as high chemical and biological stabilities has led to persistent environmental pollution, and bioaccumulation and biomagnifications in the food chains [1–4]. Moreover, studies including animal testing suggest that PCBs cause damage to the skin, thyroid, immune system, liver, and kidney, work as endocrine disruptors, and are probable carcinogens in fat-containing tissues [3,5,6]. In spite of the possible risk of PCBs to human health and the global ecosystem, only a part of the world's gross production (about 1.5 million tonnes) has so far been destroyed while other parts have been stored under strict conditions based on the laws in many countries. However, with a longer period of storage of the PCBs, the risk of improper

disposal or an accidental leak (e.g., fire, earthquake, war, and so on) has increased [7]. Therefore, PCBs are targeted for worldwide elimination by global treaty such as the Stockholm Convention on Persistent Organic Pollutants (POPs). Currently, PCBs are principally being destroyed by high-temperature incineration [8], but the high cost of transport, limitation of destruction, possible production of highly toxic substances [9], and public concerns about discharges from incinerators are strongly forcing a move to more simple, inexpensive and safe alternative methods [10]. Lots of remediation techniques currently under development include the substitution of chlorides [11,12], hydride reduction [13–17], hydrodechlorination [18–21], dechlorination using metals [22–29], mechanochemical remediation [30,31], photolysis [32–37], bioremediation [38], γ-radiolysis [39–42], oxidation [43–45], electrolysis [46–48], ultrasonics [49], super/subcritical degradation [50–52] and so on. Some of them are used industrially to mainly treat liquid PCBs and PCB-contaminated oils. However, the low reactivity and/or selectivity of most methods are manifested by the low applicability to the dechlorination of especially multi-chlorinated aromatic compounds. Furthermore, most processes require high heat, high pressure, radiation, stoichiometric or more equivalents of reagents, vast amounts of catalyst and/or strongly basic conditions with

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special facilities, but many of them are very frequently incomplete.

We have reported that the addition of a nitrogen-containing base such as NH$_3$, pyridine, and ammonium acetate to a Pd/C-catalyzed hydrogenation system as a weak catalyst poison chemoselectively inhibited the hydrogenolysis of a benzyl ether with smooth hydrogenation of the other reducible functionalities such as olefin, Cbz, benzyl ester, azide, and so on [53,54]. During the course of our further study on the chemoselective hydrogenation using a Pd/C–amine system, we found that the catalytic activity of Pd/C toward the hydrodechlorination of aromatic chlorides was remarkably and selectively enhanced by the addition of triethylamine (Et$_3$N) [55,56] and this system efficiently worked for the detoxification method of POPs such as 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p'*-DDT), [1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane] (*o,p'*-DDT) [57], and PCBs [58]. In this paper, we describe the details for the Pd/C-catalyzed hydrodechlorination of PCBs, which includes the ones from a capacitor and individual PCB congeners.

2. Experimental

2.1. Materials and chemicals

The individual PCB congeners were purchased from Accustandard, Inc. (New Heaven, CT) and used without any purification prior to use. Aroclor® 1254 and Aroclor® 1248 were manufactured by the Monsanto Chemical Co. (St. Louis, MO). PCBs from a capacitor were manufactured by the Shizuki Seisakusyo Co. (Hyogo, Japan) in 1965. Ten percent Pd/C and Et$_3$N were purchased from Sigma–Aldrich (St. Louis, MO) and Wako Pure Chemical Industries Ltd. (Osaka, Japan), respectively. MeOH (analytical grade) was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and used without any purification prior to use.

2.2. General procedure

After two vaccum/H$_2$ cycles to replace air with H$_2$ in a round-bottom flask, a suspension of the PCBs (25 mg to 50 g),
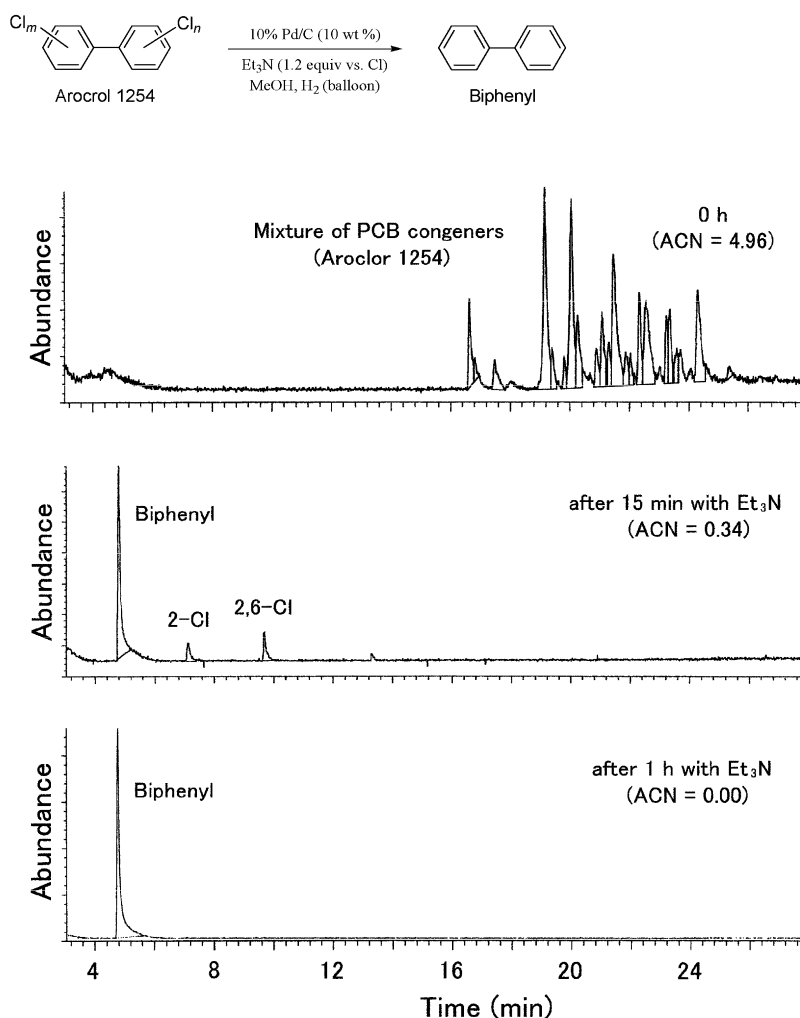

Fig. 1. Hydrodechlorination of Aroclor® 1254 with Et$_3$N. Conditions: Aroclor® 1254 (100 mg, 0.308 mmol), 10% Pd/C (10.0 mg), Et$_3$N (185 mg, 1.83 mmol), and MeOH (10 cm³), H$_2$ (balloon), room temperature.

10% Pd/C (3 or 10% of the weight of the PCBs), and Et$_3$N (1.2 equiv. for each mole of chlorine atoms in the PCBs) in MeOH (5–200 cm^3) was vigorously stirred using a stir bar under a hydrogen atmosphere (balloon) at ambient temperature (ca. 20 °C) for 1–24 h. At a given time point, the reaction mixture (1 cm^3) was sampled using a syringe, filtered through a 0.2 μm Millipore membrane filter (Millipore) or Celite pad, and concentrated in vacuo. The residue was partitioned between hexanes (10 cm^3) and H$_2$O (10 cm^3) and the organic layer was washed with brine (10 cm^3), dried (MgSO$_4$), and filtered. An aliquot (1 cm^3) was taken from the filtrate, diluted with hexanes (19 cm^3), and analyzed using a Hewlett-Packard 5891 series II gas chromatograph equipped with a Hewlett-Packard 5972 mass-selective detector (Hewlett-Packard, measurable limit = approx. 0.5 ppm) and a Neutrabond-5 capillary column (30 m × 25 m, 0.4 μm film thickness; GL Science). Helium was employed as the carrier gas at the flow rate of 1.0 mL/min. The injector and detector temperatures were 230 and 250 °C, respectively. The column temperature was programmed to ramp from 150 °C (5 min hold) to 250 °C (3 min hold) at a rate of 5 °C/min. The retention times of each congener were as follows: biphenyl, 4.77 min; 2-chlorobiphenyl, 7.08 min; 3-chlorobiphenyl, 8.64 min; 4-chlorobiphenyl, 8.86 min; 2,2′-dichlorobiphenyl, 9.65 min; 2,3-dichlorobiphenyl, 10.75 min; 2,4-dichlorobiphenyl, 10.79 min; 2,5-dichlorobiphenyl, 11.54 min; 2,6-dichlorobiphenyl, 9.69 min; 3,3′-dichlorobiphenyl, 12.92 min; 3,4-dichlorobiphenyl, 13.18 min; 3,5-dichlorobiphenyl, 12.11 min; 4,4′-dichlorobiphenyl, 13.40 min; 2,4,5-trichlorobiphenyl, 14.68 min; 2,2′,6,6′-tetrachlorobiphenyl, 14.61 min; 3,3′,4,4′-tetrachlorobiphenyl, 21.57 min; 3,3′,4,4′5-pentachlorobiphenyl, 24.63 min; 2,2′,4,4′,6,6′-hexachlorobiphenyl, 19.67 min; 3,3′, 4,4′,5,5′-hexachlorobiphenyl, 27.82 min; 2,2′,3,3′,4,6,6′-heptachlorobiphenyl, 24.09 min; 2,2′,3,3′,5,6,6′-heptachlorobiphenyl, 23.78 min.

The specific reaction conditions are as follows: in Fig. 1, Aroclor® 1254 (100 mg, 0.308 mmol), 10% Pd/C (10.0 mg), Et$_3$N (185 mg, 1.83 mmol), and MeOH (10 cm^3) were used and the reaction was completed in 1 h. In Fig. 3, Aroclor® 1254 (100 mg, 0.308 mmol), 10% Pd/C (10.0 mg), Et$_3$N (185 mg, 1.83 mmol), paraffin oil (1 cm^3) and MeOH (1 cm^3) were used and the reaction was completed in 5 h. In Fig. 4, PCBs from capacitor (500 mg, 1.87 mmol), 10% Pd/C (50.0 mg), Et$_3$N (747 mg, 7.38 mmol), and MeOH (5 cm^3) were used and the reaction was completed in 1 h. In Fig. 5, in the first run Aroclor® 1254 (500 mg, 1.54 mmol), 10% Pd/C (50.0 mg), Et$_3$N (930 mg, 9.19 mmol), and MeOH (5 cm^3) were used and 49.5 mg of 10% Pd/C was recovered. In the second run, Aroclor® 1254 (495 mg, 1.52 mmol), recovered 10% Pd/C (49.5 mg), Et$_3$N (920 mg, 9.09 mmol), and MeOH (5 cm^3) were used and 48.0 mg of 10% Pd/C was recovered. In the third run, Aroclor® 1254 (480 mg, 1.48 mmol), recovered 10% Pd/C (48.0 mg), Et$_3$N (890 mg, 8.80 mmol), and MeOH (5 cm^3) were used. In Table 1, PCBs from capacitor (50.0 g, 187 mmol), 10% Pd/C (5.00 g), Et$_3$N (74.7 g, 738 mmol), and MeOH (200 cm^3) were used and the reaction was completed in 18 h.

3. Results and discussion

3.1. Hydrodechlorination of PCBs under Pd/C–H$_2$–Et$_3$N system

Our initial study of the chemoselective hydrodechlorination of 4-chlorobiphenyl using the Pd/C–Et$_3$N system revealed that the treatment of the chloride with 10% Pd/C (3% of the substrate weight) and Et$_3$N (1.2 equiv. vs. chlorine atom) in MeOH at room temperature under ordinary hydrogen pressure (balloon) proved to be the best reaction conditions. To explore the application of our method, the hydrodechlorination of commercial PCBs (Aroclor® 1254, Monsanto Chemical Co.) which are complex mixtures of multi-chlorinated biphenyls was investigated. In accordance with the dechlorination of 4-chlorobiphenyl, triethylamine was used with 1.2 equiv. versus the average chlorination number (ACN) [16] of the PCBs and 10% Pd/C was employed with 3% of the weight of the substrate. However, the hydrodechlorination of Aroclor® 1254, which possesses an average of 4.96 chlorine atoms per molecule (ACN = 4.96), was not complete even after 24 h, with trace amount of intermediates, 2-chlorobiphenyl and 2,6-dichlorobiphenyl, detected by GC/MS. The delay of the reaction progress could be attributed to the previous experimental result that Pd/C was time-dependently poisoned by exposure to HCl and Et$_3$N·HCl, [55,56,59] which form during the hydrodechlorination. When the amount of 10% Pd/C was increased to 10% of the weight of Aroclor® 1254, the reaction was nearly completed only after 15 min (ACN = 0.34), and the GC/MS indicated the existence of a small amount of intermediates, 2-chlorobiphenyl, 2,6-dichlorobiphenyl and a trichlorobiphenyl. These intermediates were entirely dechlorinated within 1 h and the complete degradation of Aroclor® 1254 and accumulation of the resulting biphenyl as the sole product were observed (Fig. 1). Therefore, 10% Pd/C was employed with 10% of the weight of the substrate for the PCBs degradation due to safety reasons.

Moreover, Aroclor® 1248 (ACN = 3.93) was also smoothly dechlorinated within 1 h to afford the corresponding biphenyl in a 100% conversion yield (GC/MS) and no products other than biphenyl were detected by GC/MS. In contrast, the degradation of Aroclor® 1254 without Et$_3$N was quite slow (Fig. 2). Very little dechlorination was observed after 1 h (ACN = 4.48), and approximately 60% of the chlorine atoms of Aroclor® 1254 still remained even after 24 h (ACN = 2.92). These results indicated that the presence of Et$_3$N during the catalytic degradation of the PCBs under the Pd/C-catalyzed hydrogenation conditions is crucial for increasing the efficiency of the reaction. As we speculated in previous papers on the Pd/C-catalyzed hydrodechlorination of aromatic chlorides, Et$_3$N would work as a single electron donor. A single electron transfer from Et$_3$N or Pd(0) to the Pd-activated chlrobenzene ring would afford an anion radical, which could be converted to the monodechlorinated benzene by the elimination of the chloride anion and subsequent hydrogenation of the corresponding benzene radical [55,56].
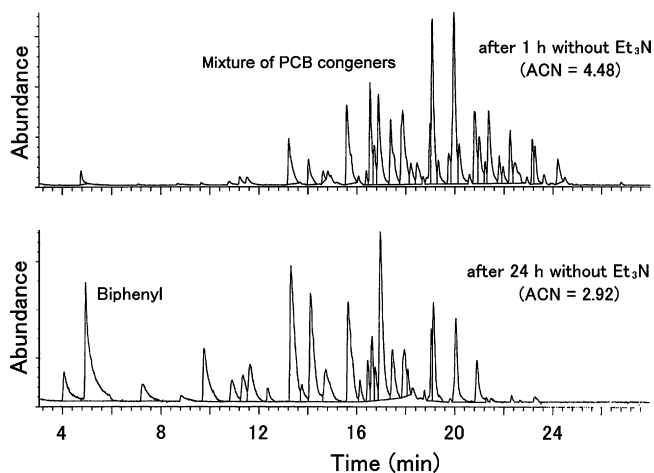
Fig. 2. Hydrodechlorination of Aroclor® 1254 without Et$_3$N. Conditions: Aroclor® 1254 (100 mg, 0.308 mmol), 10% Pd/C (10.0 mg), MeOH (10 cm^3), H$_2$ (balloon), room temperature.

3.2. Degradation of diluted PCBs in paraffin oil

Our fundamental concept to develop a safe and reliable degradation method of PCBs should be applicable to spent PCBs that have been used in devices. Therefore, we first examined PCBs diluted with paraffin oil (mineral oil) as a substrate of the hydrodechlorination because a substantial amount of the PCBs remain in existence as a diluted oil. Since the peaks derived from paraffin oil were detected in the GC chart in any time during the reaction due to its high boiling point, 2-chlorobiphenyl and 2,6-dichlorobiphenyl, intermedi-

ates of this reaction, were used as markers of the reaction's terminal point. Due to the infusibility of paraffin oil in methanol, the degradation was carried out in two phases but completed within 5 h (Fig. 3).

3.3. Degradation of PCBs from a capacitor

Furthermore, we chose undiluted PCBs, which were actually used as a high-tension capacitor oil for over 25 years as substrates. The PCBs, amber and viscous oils, mainly included dichlorobiphenyl, trichlorobiphenyl, and tetrachlorobiphenyl and possess on average 3.29 chlorine atoms per molecule (ACN = 3.29). The results of the hydrodechlorination of the capacitor oil in the presence of Et$_3$N were identical to those of Aroclor® 1254. After 1 h, the degradation was completed to afford biphenyl as the sole product (Fig. 4).

For the practical use of our method, we examined the dechlorination of PCBs from a capacitor on a large scale, that is, the reaction using 50 g of PCBs as the substrate with 200 cm^3 of methanol in a 1000 cm^3 round-bottom flask was tested. As a result, the reaction proceeded slightly slower probably because of a decrease in the stirring efficiency or/and reduced amount of hydrogen available. A trace amount of dichlorobiphenyl and monochlorobiphenyl remained after a 6 h reaction, but finally the hydrodechlorination was completed within 18 h (Table 1).

3.4. Reuse test of Pd/C

We then tried to reuse the Pd/C catalyst. After the dechlorination of Aroclor® 1254 in our Pd/C–Et$_3$N system,
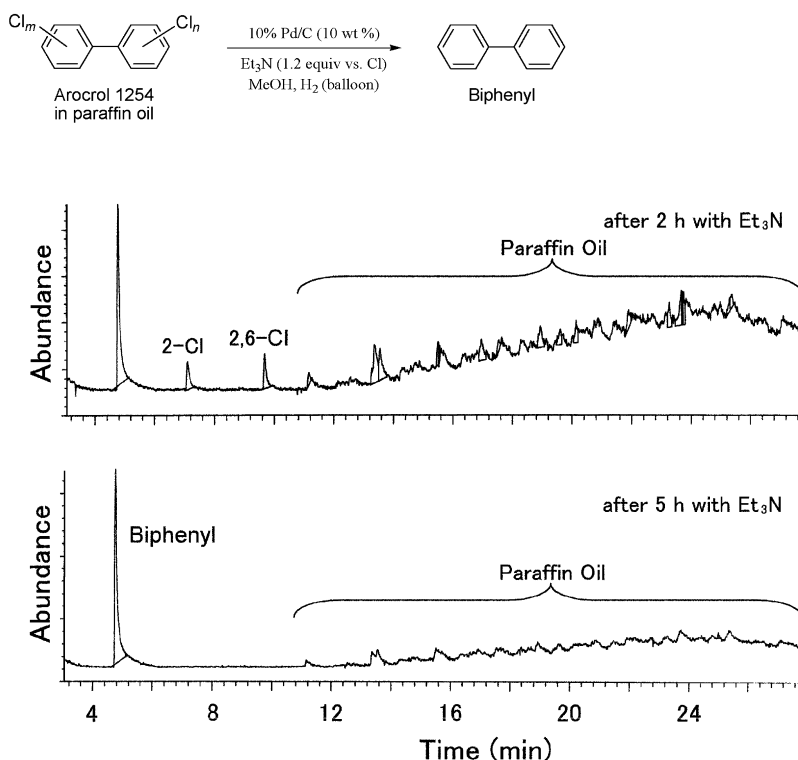

Fig. 3. Hydrodechlorination of Aroclor® 1254 in paraffin oil. Conditions: Aroclor® 1254 (100 mg, 0.308 mmol), 10% Pd/C (10.0 mg), Et$_3$N (185 mg, 1.83 mmol), paraffin oil (1 cm^3), MeOH (1 cm^3), H$_2$ (balloon), room temperature.
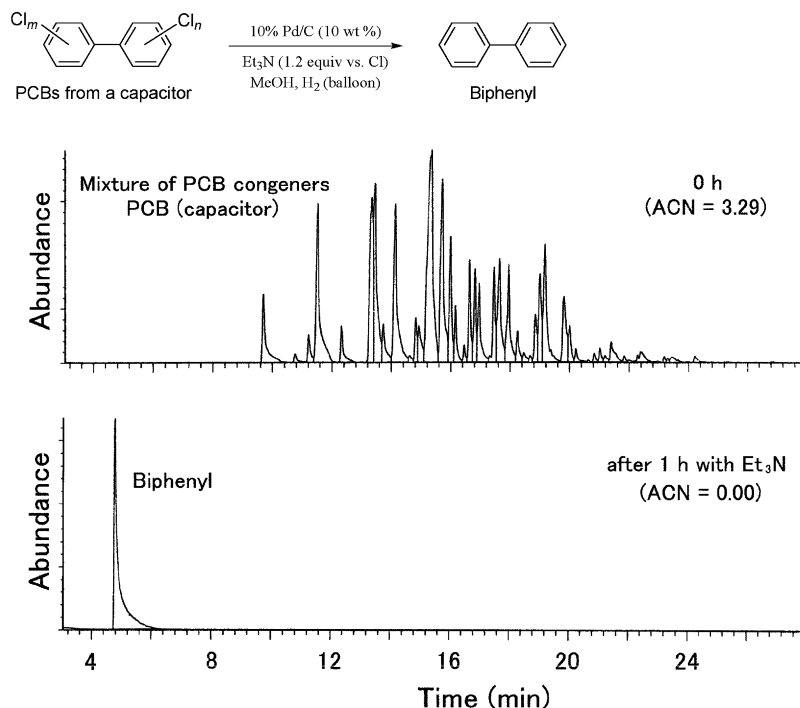
Fig. 4. Hydrodechlorination of PCBs from capacitor. Conditions: PCBs from capacitor (500 mg, 1.87 mmol), 10% Pd/C (50.0 mg), Et₃N (747 mg, 7.38 mmol), MeOH (5 cm³), H₂ (balloon), room temperature.

the catalyst was recovered by a single filtration, washed with MeOH and Et₂O, dried at room temperature for 48 h, and reused. This procedure was repeated several times. Each time, the Pd/C was quantitatively recovered, but the catalyst was gradually deactivated possibly due to the catalyst poison effect of Et₃N·HCl [55,56]; a trace amount of 2-chlorobiphenyl and 2,6-dichlorobiphenyl was detected after 3 h of dechlorination in the second and third runs (Fig. 5). These results suggest that the reactivation of Pd/C might be required for reuse at a PCB degradation plant in the future.

3.5. Hydrodechlorination of individual PCB congeners

Dechlorination of specific isomers of the PCBs may be hard depending on the substitution pattern of the chlorine atoms. The

Table 1
Hydrodechlorination of PCB (capacitor) on a large scale[a]

PCBs (%)[b]	Time (h)					
m + n	0	1	2	6	18	24
0 (Biphenyl)	0	25.3	58.4	100	100	100
1 (MonoCB)	0	16.3	12.2	Trace	0	0
2 (DiCB)	10.8	25.1	18.9	Trace	0	0
3 (TriCB)	55.0	26.9	10.5	0	0	0
4 (TetraCB)	29.0	6.4	Trace	0	0	0
5 (PentaCB)	4.8	0	0	0	0	0
6 (HexaCB)	0.4	0	0	0	0	0
Average no. of Cl	3.29	1.73	0.82	0	0	0
% Cl remaining	100	52.6	24.9	0	0	0

[a] Conditions: PCBs from capacitor (50.0 g, 187 mmol), 10% Pd/C (5.00 g), Et₃N (74.7 g, 738 mmol), MeOH (200 cm³), H₂ (balloon), room temperature.
[b] Yields were determined by GC/MS.

degradation of commercially available pure PCB congeners was then studied in detail. As a result, either monochlorobiphenyl or dichlorobiphenyl was smoothly dechlorinated with no influence by the *ortho*-, *meta*-, and *para*-substitution pattern (entries 1–11, Table 2). Trichlorobiphenyl was also similarly dechlorinated to give a biphenyl (entry 12, Table 2).

A major reason for the concern about the regulation of PCBs in the environment is their effects on biological systems. Co-planar PCB congeners that possess no chlorine atoms in the 2,2′,6, and 6′ (*ortho*-) positions of a biphenyl nucleus can be assumed to have a planar dioxin-like conformation because they lack the steric hindrance of the *ortho*-chlorines and elicit a serious dioxin-like toxicity and carcinogenicity [1–4]. For the reason that a certain amount of co-planar PCB congeners was contained in almost all PCB products during the production process, the degradation of commercially available pure co-planar PCB congeners, such as 3,3′,4,4′-tetrachlorobiphenyl, 3,3′,4,4′,5-pentachlorobiphenyl and 3,3′,4,4′,5,5′-hexachlorobiphenyl, has been studied. Under our hydrodechlorination conditions, each co-planar PCB congener was smoothly converted to biphenyl within 1 h and a mixture consisting only of biphenyl (100%) was obtained after a simple extraction process (Table 3).

On the contrary, the dechlorination of the PCB congeners that had all the *ortho*-positions of the ring-junction substituted with chlorine atoms was markedly delayed. When the fully *ortho*-substituted PCB congeners, such as 2,2′,4,4′,6,6′-hexachlorobiphenyl, 2,2′,3,3′,4,6,6′-heptachlorobiphenyl and 2,2′,3,3′,5,6,6′-heptachlorobiphenyl, were employed for the dechlorination, the chlorine atoms on the all *ortho*-positions remained, i.e., 2,2′,6,6′-tetrachlorobiphenyl was obtained as the sole product after 2 h of the hydrodechlorination (Table 4).
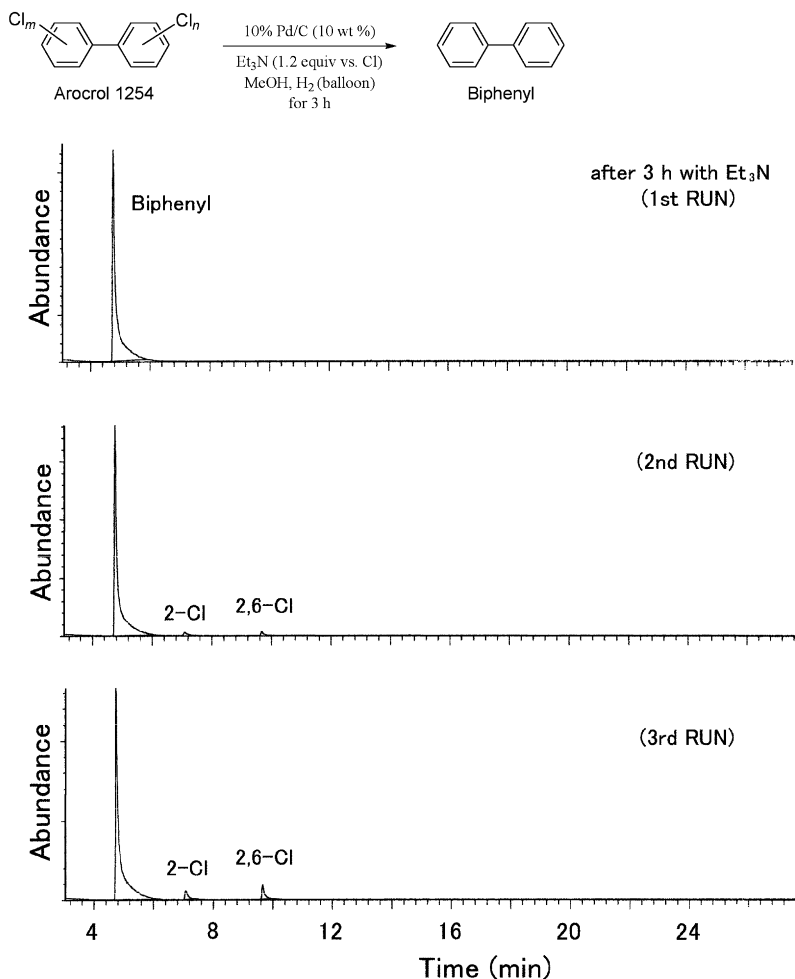
Fig. 5. Reuse test of Pd/C. Conditions: *for the first run*, Aroclor® 1254 (500 mg, 1.54 mmol), 10% Pd/C (50.0 mg), Et$_3$N (930 mg, 9.19 mmol), MeOH (5 cm^3), H$_2$ (balloon), room temperature, 3 h; *for the second run*, Aroclor® 1254 (495 mg, 1.52 mmol), recovered 10% Pd/C (49.5 mg), Et$_3$N (920 mg, 9.09 mmol), MeOH (5 cm^3), H$_2$ (balloon), room temperature, 3 h; *for the third run*, Aroclor® 1254 (480 mg, 1.48 mmol), recovered 10% Pd/C (48.0 mg), Et$_3$N (890 mg, 8.80 mmol), MeOH (5 cm^3), H$_2$ (balloon), room temperature, 3 h.

Table 2
Hydrodechlorination of individual PCB congeners[a]

Entry	Substrate	IUPAC no.	Yields of biphenyl (%)[b]
1	2-CB	1	100 (77)
2	3-CB	2	100 (73)
3	2,2′-DiCB	4	100 (87)
4	2,3-DiCB	5	100 (64)
5	2,4-DiCB	7	100 (81)
6	2,5-DiCB	9	100 (87)
7	2,6-DiCB	10	100 (88)
8	3,3′-DiCB	11	100 (53)[c]
9	3,4-DiCB	12	100 (59)
10	3,5-DiCB	14	100 (53)
11	4,4′-DiCB	15	100 (65)
12	2,4,5-TriCB	29	100 (76)

[a] Conditions: chlorinated biphenyl (22–50 mg), 10% Pd/C [3% (entries 1 and 2) or 10% (entries 3–12) of the substrate weight], Et$_3$N (1.2 equiv. for each mole of chlorine atoms of chlorinated biphenyl), MeOH (3–5 cm^3), H$_2$ (balloon), room temperature, 1 h.
[b] Yields were determined by GC/MS and isolated yields were indicated in parenthesis.
[c] Reacted for 2 h.

Furthermore, the dechlorination of 2,2′,6,6′-tetrachlorobiphenyl was investigated and showed that the chlorine atoms on the *ortho*-positions were quite stable, but the extension of the reaction time up to 24 h allowed a slow progress to give biphenyl in about 7% yield (Scheme 1) and the formation of any other intermediary products such as 2,6,6′-trichlorobiphenyl, 2,6- and 2,2′-dichlorobiphenyl, was not observed. Although these results clearly indicated that 2,2′,6,6′-tetraphenylbiphenyl is only an inactive substance for the present hydrodechlorination method, such fully *ortho*-substituted PCB congeners are only slightly contained in the commercial PCB mixture [3], since the sterically hindered 2,2′,6,6′-substituted PCBs congeners are hardly formed during the manufacturing process of the PCBs.

Two benzene rings of such biphenyls chlorine-substituted on the all *ortho*-positions should twist around each other. These chlorine atoms might cover the benzene rings and hinder the single electron transfer (SET) process from Et$_3$N or Pd(0), which we proposed as the initial step for the dechlorination using the Pd/C–Et$_3$N–H$_2$ system in our previous study [55,56].

Table 3
Hydrodechlorination of co-planar PCBs[a]
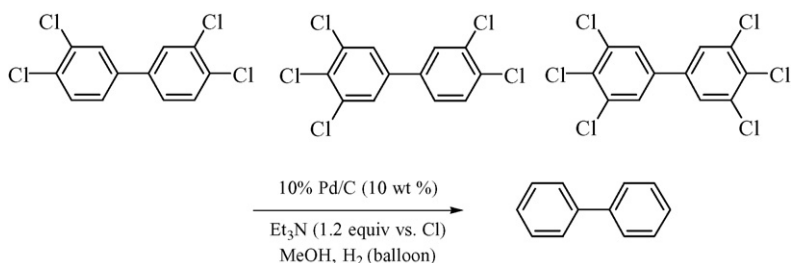
Entry	Substrate	IUPAC no.	TEF[b]	Yield (%)[c]
1	3,3′,4,4′-TetraCB	77	0.0001	100 (76)
2	3,3′,4,4′,5-PentaCB	126	0.1	100 (51)
3	3,3′,4,4′,5,5′-HexaCB	169	0.01	100 (57)

[a] Conditions: chlorinated biphenyl (3–23 mg), 10% Pd/C (10% of the substrate weight), Et$_3$N (1.2 equiv. for each mole of chlorine atoms of chlorinated biphenyl), MeOH (5 cm^3), H$_2$ (balloon), room temperature, 1 h.
[b] Toxicity equivalent factor (WHO).
[c] Yields were determined by GC/MS and isolated yields were indicated in parenthesis.

Table 4
Hydrodechlorination of fully *ortho*-substituted PCBs[a]

2,2′,6,6′-tetrachlorobiphenyl
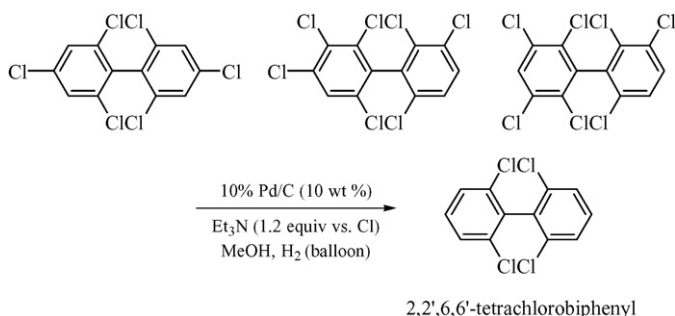
| Entry	Substrate	IUPAC no.	Yield (%)[b]
1	2,2′,4,4′,6,6′-HexaCB	155	93
2	2,2′,3,3′,4,6,6′-HeptaCB	176	100
3	2,2′,3,3′,5,6,6′-HeptaCB	179	100[c]

[a] Conditions: chlorinated biphenyl (3–25 mg), 10% Pd/C (10% of the substrate weight), Et$_3$N (1.2 equiv. for each mole of chlorine atoms of chlorinated biphenyl), MeOH (5 cm^3), H$_2$ (balloon), room temperature, 1 h.
[b] Yields were determined by GC/MS.
[c] Reacted for 2 h.

However, once one of chlorine atoms was removed from 2,2′,6,6′-tetrachlorobiphenyl, it would become much easier for the formed 2,6,6′-trichlorobiphenyl to undergo SET, leading to the smooth dechlorination of the other remaining chlorine atoms, and the other intermediates could not be detected. Therefore, Aroclor® 1254, Aroclor® 1248 and PCB (capa-citor) could be smoothly dechlorinated to afford biphenyl in a 100% conversion yield and no other products were detected within the measurable limit (approx. 0.5 ppm) of the GC/MS. The low reactivity of the fully *ortho*-substituted PCB congeners would exert little influence on the detoxification of the stored PCBs.
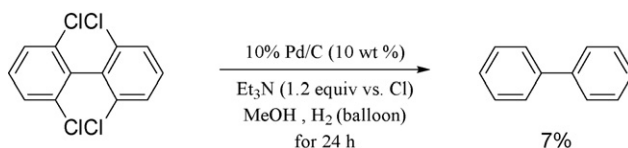
Scheme 1. Hydrodechlorination of 2,2′,6,6′-tetrachlorobiphenyl. Conditions: 2,2′,6,6′-tetrachlorobiphenyl (25.0 mg, 0.0856 mmol), 10% Pd/C (2.5 mg), Et$_3$N (0.0573 cm^3, 0.411 mmol), MeOH (5 cm^3), H$_2$ (balloon), room temperature, 24 h. Yield was determined by GC/MS.

4. Conclusions

In conclusion, the hydrodechlorination method of PCBs using the Pd/C–Et$_3$N system was accomplished under ambient hydrogen pressure and temperature. Aroclor® 1254, Aroclor® 1248, 10% Aroclor® 1254 in paraffin oil and PCBs from a capacitor could be completely dechlorinated, and no products other than biphenyl were detected by GC/MS. Nineteen pure PCB congeners were also employed for the degradation method and found to be easily dechlorinated including the highly toxic co-planar PCBs except for the fully *ortho*-substituted PCB congeners, the 2,2′,6,6′-substituted PCBs, which were not completely dechlorinated, i.e., all the chlorine atoms on the *ortho*-positions remained under the present hydrodechlorination conditions. However, the limitation of the method would not affect the degradation efficiency of the PCBs due to the slight presence of the fully *ortho*-substituted PCB congeners in the stored PCBs. The present Pd/C–Et$_3$N–H$_2$ system does not require heating, high pressure hydrogen, nor special equipment, and achieved extensive improvement in simplicity, safety, and time- and cost-efficiencies over the previously proposed chemical remediation processes of PCBs. In addition, all reagents and solvents used for the degradation reaction would be reusable, and the reaction mixture contains only biphenyl and Et$_3$N·HCl. Further study to apply the present method for practical use regarding the detoxification of stored PCBs is now ongoing in our laboratory.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2007.12.019.

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